Ni supported on γ-Al₂O₃ promoted by Ru for the dry reforming of methane in packed and monolithic reactors

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Research article

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ABSTRACT

Dry reforming (DRM) is an efficient way for CH₄ and CO₂ valorisation because the produced syn-gas has an H₂/CO ratio equal to that suitable for the synthesis of oxygenated hydrocarbons and synthetic fuels. The development of Ni (10 wt%) based structured and unstructured catalysts promoted by a small amount of Ru (0.5 wt%) for DRM has been investigated. Unstructured catalysts were prepared by wet impregnation method and a combination of wash coating-wet impregnation methods was used for cordierite monoliths. Samples were characterized by XRD, BET, H₂-TPR, TEM, FE-SEM, XPS techniques and the catalytic activity for DRM was evaluated in the temperature range 600–800 °C. The catalyst stability was followed at 800 °C during time on steam. Ru promoted catalyst (Ni-Ru) was remarkable active and stable whereas Ni catalyst deactivated due to the formation of NiO (Eq. 4) containing inactive phases. Ni-Ru monolith was initially much more active than monometallic Ni stating the positive effect of Ru on maintaining Ni reduced. Reaching steady state condition, Ni rapidly deactivated due to carbon formation, whereas Ni-Ru monolith remained stable confirming that Ru behaves as an efficient and cheap promoter of Ni for DRM.

To achieve suitable CH₄ and CO₂ conversions, DRM is operated at high temperature (generally above 700 °C). In that condition, the Boudouard reaction is thermodynamically unfavoured and the RWGS is suppressed by the low CO₂ concentration. While, the deposition of carbon may not be completely avoided affecting the long term operation of the catalysts therefore, there is a pressing need to increase the catalysts resistance toward carbon deposition.

Ni-based catalysts are so far the most active, but also highly prone to carbon formation, because, together with the ability to activate the C–H bond, Ni has a high affinity to carbon [5]. In the search of active and stable Ni-based catalysts, several approaches have been explored: a) the stabilization of small Ni particles which have low catalytic activity toward the C–H cracking [6,7]; b) the addition of another metal resulting in the formation of less C-sensitive alloys or in the increase of Ni dispersion [8–10]; c) the use of supports which may activate CO₂

CH₄→C + 2H₂, ΔH°₂₉₈ K = 75 kJ mol⁻¹ (3)

2CO→C + CO₂, ΔH°₂₉₈ K = −172 kJ mol⁻¹ (4)

1. Introduction

The CO₂ reforming of CH₄ (Eq. (1)) or dry reforming (DRM) is as an efficient way for the CH₄ and CO₂ valorisation [1–4]. In the produced syn-gas the H₂/CO ratio is equal to that suitable for the synthesis of oxygenated hydrocarbons and synthetic fuels.

CH₄ + CO₂→(2)H₂ + 2CO, ΔH°₂₉₈ K = 247 kJ mol⁻¹ (1)

To date, the DRM industrial implementation is mainly impeded by the co-occurrence of the reverse water gas shift reaction (RWGS) (Eq. (2)), the catalyst deactivation and/or reactor plugging due methane cracking (Eq. (3)) and the Boudouard reaction (Eq. (4)).

H₂ + CO₂→(3)CO + H₂O, ΔH°₂₉₈ K = 41 kJ mol⁻¹ (2)

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The reactant conversions of Ni-Ru deposited on cordierite monolith were higher in comparison to packed bed reactor (unstructured catalyst) due to the larger contact time. The initial conversions of Ni-Ru monolith were much more higher than the corresponding monometallic Ni, further confirming the positive effect of Ru on maintaining Ni reduced. Ni monolith required a long time to reach steady state condition and rapidly deactivated due to carbon formation. While, Ni-Ru monolith remained stable after reaching steady state condition.

Morphological analysis confirmed that a large amount of carbon filament was deposited on monometallic Ni mainly by a tip growth mechanism, whereas on Ni-Ru, only few carbon filaments were deposited with a base growth mechanism primarily in the inlet region. Thus, Ru behaved as an efficient and cheap promoter of Ni based catalyst. Finally, from the distribution of carbon deposits on monolith, a zone coating may further increase the operating time of the reactor.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2016.12.015.

References


Table 3

<table>
<thead>
<tr>
<th>Sampling areas</th>
<th>C wt% Ni–M</th>
<th>C wt% Ni–Ru–M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>34.73</td>
<td>22.55</td>
</tr>
<tr>
<td>Middle</td>
<td>30.98</td>
<td>6.91</td>
</tr>
<tr>
<td>Outlet</td>
<td>20.33</td>
<td>3.36</td>
</tr>
</tbody>
</table>